



JC14 Rec'd PCT/PTO 30 APR 2002

PCT

CERTIFICATE OF HAND DELIVERY

I hereby certify that this correspondence is being hand filed with the United States Patent and Trademark Office in Washington, D.C. on

30 April 2002.

Name: Shari Hall White

Attorney Docket No. 220772010340

**PATENT COOPERATION TREATY
IN THE UNITED STATES RECEIVING OFFICE**

In the PCT application of:

CATALYTICA ENERGY SYSTEMS, INC.

International Application No.: Not Yet Assigned ✓

International Filing Date: 26 October 2001

Title: METHOD OF THERMAL NO_x REDUCTION IN
CATALYTIC COMBUSTION SYSTEMS

**PETITION FOR CORRESPONDENCE NEVER RECEIVED PURSUANT TO
37 CFR §1.10(e) (No Fee Required)**

Assistant Commissioner for Patents
Box PCT
Washington, D.C. 20231

Attn: RO/US

Dear Sir or Madam:

In connection with the above-identified PCT application, Applicant hereby promptly submits a petition with relation to Correspondence Never Received pursuant to 37 CFR §1.10(e).

It is hereby acknowledged that the above application was deposited on 26 October 2001, by previous agent of record, Innovation Law Group, Ltd. Application has subsequently been transferred to Morrison & Foerster LLP, for further prosecution. It was noted by Morrison & Foerster LLP, that a Notification of Application Number and Filing Date was not received for this application. Upon conversing with the PCT Help Desk at the RO/US, it was pointed out that

the Office showed no record of this application having been received and recommended that we file a Petition under 37 CFR 1.10(e) as soon as possible.

Accordingly, Applicant further petitions for a filing date as of the date of deposit with the U.S. Postal Service (USPS), where correspondence deposited as "Express Mail" is never received by the Office.

Applicant's undersigned attorney submits the following:

1. Transmittal Letter to the United States Receiving Office concerning a filing under 37 CFR §1.10 dated 26 October 2001 (26.10.01 - date of deposit).
2. A copy of "Express Mail" label No. **EL 719 275 624 US**, showing the "date in" with a Los Altos, CA Post Station Office - postmarked date of **October 26, 2001** addressed to Asst. Commissioner for Patents, Box PCT, Washington DC 20231.
3. Copy of PCT Request Form (7 pages); PCT Fee Calculation Sheet (1 page); Description (11 pages); Claims (3 pages); Abstract (1 page); and Formal Drawings (4 pages).
4. Copy of USPS Shipment History--This notice clearly shows that the application was deposited and accepted by the Post Office on 26 October 2001.
5. Copy of Check No. 1528, in the amount of \$1,594, which accompanied the application to cover all related PCT filing fees.
6. Copy of Statement of Account which shows that check number 1528, in the amount of \$1,594, was deposited and cleared the account, indicating that the Office received the correspondence within the Express Mail envelope.

In view of the submission of the above documents, Applicant respectfully requests the United States Patent and Trademark Office to accept the filing of the above-mentioned international patent application and to show the filing date as being **26 October 2001 (26.10.01)** pursuant to the Express Mail label postmarked by the Los Altos, CA post office as mentioned above.

Applicant further requests that the United States Patent and Trademark Office send the confirmation of filing date and a PCT serial number assigned to this application, to the undersigned attorney below. As this case was transferred to our firm, we enclose a PCT General Power of Attorney signed by the Applicant.

No additional fee is deemed necessary in connection with the filing of this Petition.

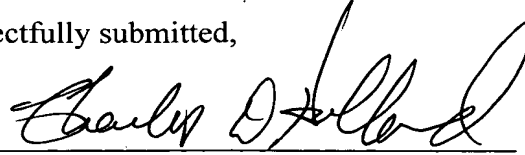
If any issues remain in connection with the filing of this Petition and fulfillment of the requirements under 37 CFR 1.10(e), the Office is invited to contact the undersigned attorney at (650) 813-5832.

We thank you for your prompt attention to this urgent matter.

Respectfully submitted,

Dated: 29 April 2002

By:



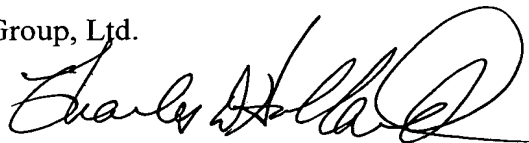
Charles D. Holland, No. 35,196

Morrison & Foerster LLP
755 Page Mill Road
Palo Alto, California 94304-1018
Telephone: (650) 813-5600
Facsimile: (650) 494-0792

DECLARATION OF CHARLES D. HOLLAND

I, Charles D. Holland, the newly appointed agent of record, hereby declare that the attached copies of all correspondence and proofs of filing are true copies of what is contained in our file copy, and received from Innovation Law Group, Ltd.

Dated: 29 April 2002

A handwritten signature in black ink, appearing to read "Charles D. Holland", written over a horizontal line.

Charles D. Holland, Esq.

PCT

GENERAL POWER OF ATTORNEY

(for several international applications filed under the Patent Cooperation Treaty)
(PCT Rule 90.5)

The undersigned applicant(s)

(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.):

CATALYTICA ENERGY SYSTEMS, INC.

430 Ferguson Drive

Mountain View, California 94043-5272

United States of America

hereby appoint(s) the following person as:

☒ agent ☐ common representative

Morrison & Foerster LLP
755 Page Mill Road
Palo Alto, California 94304-1018
United States of America
Telephone: (650) 813-5600
Facsimile: (650) 494-0792

Lisa A. Amii, Randolph Ted Apple, Mehran Arjomand, Laurie A. Axford, Sanjay S. Bagade, Erwin J. Basinski, Shantanu Basu, Richard R. Batt, Vincent J. Belusko, Jonathan Bockman, Kimberly A. Bolin, Barry E. Bretschneider, Tyler S. Brown, Nicholas Buffinger, A. Randall Camacho, Mark R. Carter, Robert K. Cerpa, Peng Chen, Alex Chartove, Thomas Chuang, Thomas E. Ciotti, Cara M. Coburn, Matthew M. D'Amore, Raj S. Davé, Peter Davis, Karen B. Dow, Stephen C. Durant, Carolyn A. Favorito, David L. Fehrman, Hector Gallegos, Thomas George, Debra J. Glaister, Kenneth R. Glick, Bruce D. Grant, Johny U. Han, Douglas G. Hodder, Alan S. Hodes, Charles D. Holland, Kelvan P. Howard, Peter Hsieh, Jill A. Jacobson, Wayne Jaeschke, Jr., Madeline I. Johnston, Parisa Jorjani, Ararat Kapouytian, Richard C. Kim, Cameron A. King, Lawrence B. Kong, Kawai Lau, Glenn Kubota, Rimas T. Lukas, Michael J. Mauriel, Gladys H. Monroy, Philip A. Morin, Kate H. Murashige, Paul S. Naik, Mabel Ng, Martin M. Noonan, Catherine M. Polizzi, Phillip Reilly, Robert E. Scheid, Debra A. Shetka, Terri Shieh-Newton, Rebecca Shortle, Kevin R. Spivak, Stanley H. Thompson, Thomas L. Treffert, Brenda J. Wallach, Michael R. Ward, E. Thomas Wheelock, Todd W. Wight, Frank Wu, David T. Yang, Peter J. Yim, George C. Yu, Karen R. Zachow

to represent the undersigned before ☒ all the competent International Authorities
☐ the International Search Authority only
☐ the International Preliminary Examining Authority only

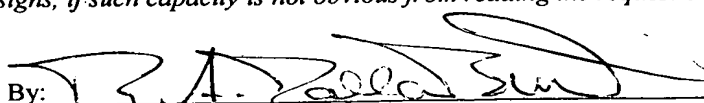
in connection with any and all international applications filed by the undersigned with the following Office United States as receiving Office and to make or receive payments on behalf of the undersigned.

Signature of the applicant(s)

(where there are several persons, each of them must sign; next to each signature indicate the name of the person signing and the capacity in which the person signs, if such capacity is not obvious from reading the request or this power):

Date: November 10, 2001

By:



Name: Ralph A. Dalla Betta

Title: Vice President

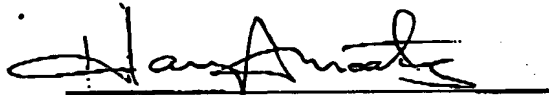
**UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE OFFICE OF ENROLLMENT AND DISCIPLINE**

LIMITED RECOGNITION UNDER 37 CFR §10.9(b)

David R. Heckadon is hereby given limited recognition under 37 CFR §10.9(b), as an employee of the Townsend and Townsend and Crew, law firm, to prepare and prosecute patent applications and to represent patent applicants wherein the patent applicants are clients of the Townsend and Townsend and Crew law firm, and wherein a registered practitioner who is a member of the Townsend and Townsend and Crew law firm is the attorney or agent of record. This limited recognition shall expire on the date appearing below, or when whichever of the following events first occurs prior to the date appearing below: (i) David R. Heckadon ceases to lawfully reside in the United States; (ii) David R. Heckadon's employment with the Townsend and Townsend and Crew law firm ceases or is terminated; or (iii) David R. Heckadon ceases to remain or reside in the United States on an H-1B visa.

This document constitutes proof of such recognition. The original of this document is on file in the Office of Enrollment and Discipline of the U.S. Patent and Trademark Office.

Expires: July 12, 2002



**Harry I. Moatz
Director of Enrollment and Discipline**



INNOVATION LAW GROUP, LTD. 06-00
"TRANSFORMING IDEAS INTO BUSINESS ASSETS"
GENERAL OPERATING ACCOUNT
 851 FREMONT AVE, SUITE 101
 LOS ALTOS, CA 94024
 (650) 947-7287

WASHINGTON MUTUAL BANK, F.A.
LOS ALTOS FINANCIAL CENTER 1308
 199 MAIN STREET
 LOS ALTOS, CA 94022
 90-7162/3222

1528

10/26/2001

Y TO THE
 DER OF Commissioner of Patents & Trademarks

\$ **1,594.00

One Thousand Five Hundred Ninety-Four and 00/100*****

DOLLARS

Commissioner of Patents & Trademarks
 Washington, D.C. 20231

MO 7101-012 PCT - PCT Application Filing Fee

Melinda Guion

⑈001528⑈ ⑆322271627⑆388⑈026746⑈0⑈

INNOVATION LAW GROUP, LTD. / "TRANSFORMING IDEAS INTO BUSINESS ASSETS" / GENERAL OPERATING ACCOUNT

Commissioner of Patents & Trademarks

10/26/2001

1528

7101-012 PCT - PCT Application Filing Fee

1,594.00

To the US/RO: Please place your "Received" stamp
 below and return this Self Addressed Postage Paid
 Return Receipt Postcard to us.

Atty. Docket No.: 7101-012 PCT
 Return Receipt Postcard
 Transmittal Letter - 1 pgs. (+ copy)
 Power Of Attorney - 1 pg. (Executed)
 PCT Request - 7 pgs.
 Fee Calculation Sheet - 1 pg.
 Description - 11 pgs.
 Claims - 3 pgs.
 Abstract - 1 pg.
 Drawings - 4 pgs. Figs 1-8 (Formal)
 Check # 1528 in the amount of \$1,594
 Express Mail No.: EL 719 275 624 US
 Date Mailed: October 26, 2001

1,594.00

Washington Mutual**STATEMENT OF ACCOUNT**

70,206

EM-E-B1

INNOVATION LAW GROUP, LTD.
851 FREMONT AVE STE 101
LOS ALTOS CA 94024-5602

STATEMENT PERIOD:
FROM 01-01-02
THRU 01-31-02

BASIC BUSINESS CHECKING

(Continued from Previous Page)

ELECTRONIC & MISCELLANEOUS WITHDRAWALS (Continued)

Date	Amount	Description
01-30		
	\$36,200.35	12 Items

CHECKS

* Indicates check out of sequence

Check Number	Amount	Date	Check Number	Amount	Date
1527	370.00	01-16	1639	623.38	01-10
1528	1,594.00	01-16	1640	100.00	01-10
1536*	627.00	01-16	1641	108.51	01-16
1571*	650.00	01-22	1643*	450.00	01-25
1615*	1,000.00	01-17	1644	213.00	01-17
1622*	463.60	01-03	1647*	492.22	01-11
1626*	13.79	01-09	1648	23.51	01-28
1627	26.90	01-09	1650*	39.00	01-28
1628	438.79	01-10	1651	101.00	01-22
1629	30.03	01-09	1652	39.58	01-22
1630	7,172.16	01-07	1653	327.77	01-24
1631	153.00	01-04	1654	144.00	01-28
1632	1,250.00	01-15	1655	59.53	01-29
1633	3,368.89	01-10	1658*	1,043.02	01-28
1637*	70.00	01-10	1659	86.15	01-31
1638	58.65	01-14	1661*	200.88	01-29
	\$21,338.36	32 Paid Items			

SERVICE FEE INFORMATION

Account Summary 01-01-2002 through 01-31-2002

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Shipping center *Track & Confirm*

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Delivery Confirmation
Signature Confirmation

Keyword/Search

Shipment History

You entered EL71 9275 624U S

Your item was delivered at 7:27 am on January 08, 2002 in WASHINGTON, DC 20231 to PATENTS. The item was signed for by M BOSTON.

Here is what happened earlier:

- NOTICE LEFT, January 07, 2002, 7:52 pm, WASHINGTON, DC 20231
- ARRIVAL AT UNIT, January 07, 2002, 7:42 pm, WASHINGTON, DC 20066
- ACCEPTANCE, October 26, 2001, 4:36 pm, LOS ALTOS, CA 94024

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JC14 Rec'd PCT/PTO 30 APR 2002

**TRANSMITTAL LETTER TO THE
UNITED STATES RECEIVING OFFICE**

Date	26 October 2001
International Application No.	PCT/US 01/012
Attorney Docket No.	7101-012 PC1

I. Certification under 37 CFR 1.10 (if applicable)

EL 719 275 624 US
Express Mail mailing number

26 October 2001
Date of Deposit

I hereby certify that the application/correspondence attached hereto is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Assistant Commissioner for Patents, Washington, D.C. 20231.


Signature of person mailing correspondence

Melissa Harrison
Typed or printed name of person mailing correspondence

II. ☒ New International Application

TITLE	METHOD OF THERMAL NOx REDUCTION IN CATALYTIC COMBUSTION SYSTEMS
-------	---

Earliest priority date (Day/Month/Year)
27 October 2000

SCREENING DISCLOSURE INFORMATION: In order to assist in screening the accompanying international application for purposes of determining whether a license for foreign transmittal should and could be granted and for other purposes, the following information is supplied. (Note: check as many boxes as apply):

- A. ☐ The invention disclosed was not made in the United States.
- B. ☐ There is no prior U.S. application relating to this invention.
- C. ☒ The following prior U.S. application(s) contain subject matter which is related to the invention disclosed in the attached international application. (NOTE: priority to these applications may or may not be claimed on form PCT/RO/101 (Request) and this listing does not constitute a claim for priority.)

application no.	60/244,019	filed on	27 October 2000
application no.	09/942,976	filed on	29 August 2001

- D. ☒ The present international application contains additional subject matter not found in the prior U.S. application(s) identified in paragraph C. above. The additional subject matter is found on pages 9 and 10 and ☒ DOES NOT ALTER ☐ MIGHT BE CONSIDERED TO ALTER the general nature of the invention in a manner which would require the U.S. application to have been made available for inspection by the appropriate defense agencies under 35 U.S.C. 181 and 37 CFR 5.1. See 37 CFR 5.15

III. ☐ A Response to an Invitation from the RO/US. The following document(s) is(are) enclosed:

- A. ☐ A Request for An Extension of Time to File a Response
- B. ☐ A Power of Attorney (General or Regular)
- C. ☐ Replacement pages:

pages		of the request (PCT/RO/101)	pages		of the figures
pages		of the description	pages		of the abstract
pages		of the claims			

- D. ☐ Submission of Priority Documents

Priority document		Priority document	
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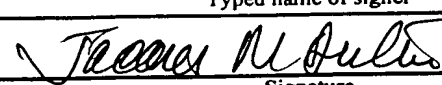
- E. ☐ Fees as specified on attached Fee Calculation sheet form PCT/RO/101 annex

IV. ☐ A Request for Rectification under PCT 91 ☐ A Petition ☐ A Sequence Listing Diskette

V. ☐ Other (please specify):

The person signing this form is the:

<input type="checkbox"/> Applicant
<input checked="" type="checkbox"/> Attorney/Agent (Reg. No.) <u>24,067</u>
<input type="checkbox"/> Common Representative

Jacques M. Dulin
Typed name of signer

Signature

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

Inter

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) 7101-012 PCT

Box No. I TITLE OF INVENTION
METHOD OF THERMAL NO_x REDUCTION IN CATALYTIC COMBUSTION SYSTEMS

Box No. II APPLICANT ☐ This person is also inventor

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Catalytica Energy Systems, Inc.
430 Ferguson Drive
Mountain View, CA 94043 US

Telephone No.
650-947-7287

Facsimile No.
650-947-7280

Teleprinter No.

Applicant's registration No. with the Office

State (that is, country) of nationality:
US

State (that is, country) of residence:
US

This person is applicant for the purposes of: ☒ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Ralph Dalla Betta
865 Doverton Square
Mountain View, CA 94043 US

This person is:

☐ applicant only
☐ applicant and inventor
☒ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒ agent ☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

Jacques M. Dulin
Innovation Law Group, Ltd.
851 Fremont Avenue, Suite 101
Los Altos, CA 94024 US

Telephone No.
650-947-7287

Facsimile No.
650-947-7280

Teleprinter No.

Agent's registration No. with the Office
24,067

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)*If none of the following sub-boxes is used, this sheet should not be included in the request.*

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Marco A. Velasco
1476 Edsel Drive
Milpitas, CA 95035 US

This person is:

- ☐ applicant only
☐ applicant and inventor
☒ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

☐ all designated States☐ all designated States except the United States of America☐ the United States of America only☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

David K. Yee
29070 Sebring Court
Hayward, CA 94544 US

This person is:

- ☐ applicant only
☐ applicant and inventor
☒ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

☐ all designated States☐ all designated States except the United States of America☐ the United States of America only☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Sarento G. Nickolas
1569 Park Ridge Drive
San Jose, CA 95118 US

This person is:

- ☐ applicant only
☐ applicant and inventor
☒ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

☐ all designated States☐ all designated States except the United States of America☐ the United States of America only☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only
☐ applicant and inventor
☐ inventor only (If this check-box is marked, do not fill in below.)

Applicant's registration No. with the Office

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

☐ all designated States☐ all designated States except the United States of America☐ the United States of America only☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No. V DESIGNATION OF STATES

Mark the applicable check-boxes below; at least one must be marked.

The following designations are hereby made under Rule 4.9(a):

Regional Patent

- ☐ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, CH & LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | | |
|--|---|---|
| <input type="checkbox"/> AE United Arab Emirates | <input type="checkbox"/> GH Ghana | <input type="checkbox"/> MX Mexico |
| <input type="checkbox"/> AG Antigua and Barbuda | <input type="checkbox"/> GM Gambia | <input type="checkbox"/> MZ Mozambique |
| <input type="checkbox"/> AL Albania | <input type="checkbox"/> HR Croatia | <input type="checkbox"/> NO Norway |
| <input type="checkbox"/> AM Armenia | <input type="checkbox"/> HU Hungary | <input type="checkbox"/> NZ New Zealand |
| <input type="checkbox"/> AT Austria | <input type="checkbox"/> ID Indonesia | <input type="checkbox"/> PL Poland |
| <input type="checkbox"/> AU Australia | <input type="checkbox"/> IL Israel | <input type="checkbox"/> PT Portugal |
| <input type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> IN India | <input type="checkbox"/> RO Romania |
| <input type="checkbox"/> BA Bosnia and Herzegovina | <input type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> RU Russian Federation |
| <input type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> JP Japan | |
| <input type="checkbox"/> BG Bulgaria | <input type="checkbox"/> KE Kenya | <input type="checkbox"/> SD Sudan |
| <input type="checkbox"/> BR Brazil | <input type="checkbox"/> KG Kyrgyzstan | <input type="checkbox"/> SE Sweden |
| <input type="checkbox"/> BY Belarus | <input type="checkbox"/> KP Democratic People's Republic of Korea | <input type="checkbox"/> SG Singapore |
| <input type="checkbox"/> BZ Belize | <input checked="" type="checkbox"/> KR Republic of Korea | <input type="checkbox"/> SI Slovenia |
| <input checked="" type="checkbox"/> CA Canada | <input type="checkbox"/> KZ Kazakhstan | <input type="checkbox"/> SK Slovakia |
| <input type="checkbox"/> CH & LI Switzerland and Liechtenstein | <input type="checkbox"/> LC Saint Lucia | <input type="checkbox"/> SL Sierra Leone |
| <input checked="" type="checkbox"/> CN China | <input type="checkbox"/> LK Sri Lanka | <input type="checkbox"/> TJ Tajikistan |
| <input type="checkbox"/> CO Colombia | <input type="checkbox"/> LR Liberia | <input type="checkbox"/> TM Turkmenistan |
| <input type="checkbox"/> CR Costa Rica | <input type="checkbox"/> LS Lesotho | <input type="checkbox"/> TR Turkey |
| <input type="checkbox"/> CU Cuba | <input type="checkbox"/> LT Lithuania | <input type="checkbox"/> TT Trinidad and Tobago |
| <input type="checkbox"/> CZ Czech Republic | <input type="checkbox"/> LU Luxembourg | <input type="checkbox"/> TZ United Republic of Tanzania |
| <input type="checkbox"/> DE Germany | <input type="checkbox"/> LV Latvia | <input type="checkbox"/> UA Ukraine |
| <input type="checkbox"/> DK Denmark | <input type="checkbox"/> MA Morocco | <input type="checkbox"/> UG Uganda |
| <input type="checkbox"/> DM Dominica | <input type="checkbox"/> MD Republic of Moldova | <input type="checkbox"/> US United States of America |
| <input type="checkbox"/> DZ Algeria | | |
| <input type="checkbox"/> EC Ecuador | <input type="checkbox"/> MG Madagascar | <input type="checkbox"/> UZ Uzbekistan |
| <input type="checkbox"/> EE Estonia | <input type="checkbox"/> MK The former Yugoslav Republic of Macedonia | <input type="checkbox"/> VN Viet Nam |
| <input type="checkbox"/> ES Spain | <input type="checkbox"/> MN Mongolia | <input type="checkbox"/> YU Yugoslavia |
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Check-boxes below reserved for designating States which have become party to the PCT after issuance of this sheet:

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Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM

The priority of the following earlier application(s) is hereby claimed:

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 27 October 2000	60/244,019	US		
item (2) 29 August 2001	09/942,976	US		
item (3)				
item (4)				
item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of this international application is the receiving Office) identified above as:

☐ all items
 ☒ item (1)
 ☒ item (2)
 ☐ item (3)
 ☐ item (4)
 ☐ item (5)
 ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(ii)):

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / US

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

Box No. VIII DECLARATIONS

The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):

Number of
declarations

- | | | |
|--|--|---|
| <input type="checkbox"/> Box No. VIII (i) | Declaration as to the identity of the inventor | : |
| <input checked="" type="checkbox"/> Box No. VIII (ii) | Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent | : |
| <input checked="" type="checkbox"/> Box No. VIII (iii) | Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application | : |
| <input type="checkbox"/> Box No. VIII (iv) | Declaration of inventorship (only for the purposes of the designation of the United States of America) | : |
| <input type="checkbox"/> Box No. VIII (v) | Declaration as to non-prejudicial disclosures or exceptions to lack of novelty | : |

Box No. VIII (ii) DECLARATION: ENTITLEMENT TO APPLY FOR AND BE GRANTED A PATENT

The declaration must conform to the standardized wording provided for in Section 212; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (ii). If this Box is not used, this sheet should not be included in the request.

Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent (Rules 4.17(ii) and 51bis.1(a)(ii)), in a case where the declaration under Rule 4.17(iv) is not appropriate:

In relation to this International Application:

Catalytica Energy Systems, Inc. is entitled to apply for and be granted a patent by virtue of the following:

All inventors have executed assignments dated March 5, 2001 and October 26, 2001, assigning all rights in the priority applications, the US Provisional and Regular Applications, and in all foreign and PCT applications to Catalytica Energy Systems, Inc.

This Declaration is made for the purposes of all Designations, except the Designation of the United States of America, if any.

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (ii)".

Box No. VIII (iii) DECLARATION: ENTITLEMENT TO CLAIM PRIORITY

The declaration must conform to the standardized wording provided for in Section 213; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (iii). If this Box is not used, this sheet should not be included in the request.

Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application specified below, where the applicant is not the applicant who filed the earlier application or where the applicant's name has changed since the filing of the earlier application (Rules 4.17(iii) and 51bis.1(a)(iii)):

In relation to this International Application:

Catalytica Energy Systems, Inc. is entitled to claim priority of earlier applications 60/242,039 and 09/924,227 by virtue of the following:

Both inventors have executed assignments dated March 5, 2001 and October 26, 2001, assigning all rights in the priority applications, the US Provisional and Regular Applications, and in all foreign and PCT applications to Catalytica Energy Systems, Inc.

This Declaration is made for the purposes of all Designations, except the Designation of the United States of America, if any.

☐ This declaration is continued on the following sheet, "Continuation of Box No. VIII (iii)".

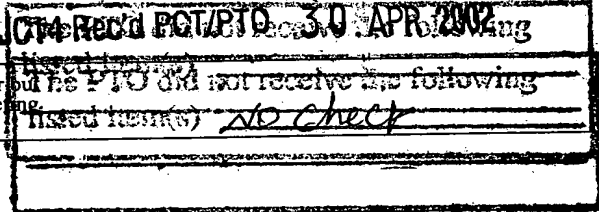
Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:		This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):	Number of items
(a) the following number of sheets in paper form:			
request (including declaration sheets)	: 7	1. <input checked="" type="checkbox"/> fee calculation sheet	: 1
description (excluding sequence listing part)	: 11	2. <input checked="" type="checkbox"/> original separate power of attorney	: 1
claims	: 3	3. <input type="checkbox"/> original general power of attorney	:
abstract	: 1	4. <input type="checkbox"/> copy of general power of attorney; reference number, if any:	:
drawings	: 4	5. <input type="checkbox"/> statement explaining lack of signature	:
Sub-total number of sheets	: 26	6. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s):	:
sequence listing part of description (actual number of sheets if filed in paper form, whether or not also filed in computer readable form; see (b) below)	: N/A	7. <input type="checkbox"/> translation of international application into (language):	:
Total number of sheets	: 26	8. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material	:
(b) sequence listing part of description filed in computer readable form		9. <input type="checkbox"/> sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other))	:
(i) <input type="checkbox"/> only (under Section 801(a)(i))		(i) <input type="checkbox"/> copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)	:
(ii) <input type="checkbox"/> in addition to being filed in paper form (under Section 801(a)(ii))		(ii) <input type="checkbox"/> (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter	:
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which the sequence listing part is contained (additional copies to be indicated under item 9(ii), in right column):		(iii) <input type="checkbox"/> together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column	:
Figure of the drawings which should accompany the abstract	: 6	10. <input type="checkbox"/> other (specify):	:
Language of filing of the international application: ENGLISH			

Box No. X SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Jacques M. Dulin
Jacques M. Dulin

For receiving Office use only		For International Bureau use only	
1. Date of actual receipt of the purported international application:		2. Drawings:	
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		<input type="checkbox"/> received:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):		<input type="checkbox"/> not received:	
5. International Searching Authority (if two or more are competent): ISA /		6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid	

Date of receipt of the record copy by the International Bureau:

This sheet is not part of and does not count as a sheet of the international application.

PCT

FEE CALCULATION SHEET
Annex to the Request

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International Application No.

Applicant's or agent's
file reference 7101-012 PCT

Date stamp of the receiving Office

Applicant

Catalytica Energy Systems, Inc.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE 240 T
2. SEARCH FEE 450 S

International search to be carried out by US
(If two or more International Searching Authorities are competent to carry out the international search, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

Where item (b) of Box No. IX applies, enter Sub-total number of sheets } 26
Where item (b) of Box No. IX does not apply, enter Total number of sheets }

b1 first 30 sheets 382 b1

b2 N/A x 9 = N/A b2
number of sheets in excess of 30 fee per sheet

b3 additional component (only if sequence listing part of description is filed in computer readable form under Section 801(a)(i), or both in that form and on paper, under Section 801(a)(ii)):

400 x N/A = N/A b3
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Add amounts entered at b1, b2 and b3 and enter total at B 382 B

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The international application contains 7 designations.

6 x 82 = 492 D
number of designation fees payable (maximum 6) amount of designation fee

Add amounts entered at B and D and enter total at I 874 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the total to be entered at I is 25% of the sum of the amounts entered at B and D.)

4. FEE FOR PRIORITY DOCUMENT (if applicable) 30 P

5. TOTAL FEES PAYABLE 1594

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TOTAL

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

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☒ cheque ☐ bank draft ☐ revenue stamps ☐ other (specify):

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☒ (This check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.
☐ Authorization to charge the fee for priority document.

Receiving Office: RO/ US
Deposit Account No.: 04-1699
Date: 26 October 2001
Name: Jacques M. Dulin
Signature: Jacques M. Dulin

**TITLE: METHOD OF THERMAL NO_x REDUCTION
IN CATALYTIC COMBUSTION SYSTEMS**

**INVENTORS: RALPH A. DALLA BETTA
MARCO A. VELASCO
DAVID K. YEE
SARENTO G. NICKOLAS**

Field of the Invention:

The invention relates to methods and apparatus, both devices and systems, for control of NO_x in catalytic combustion systems, and more particularly to control of NO_x produced downstream of the catalytic reaction zone of a combustor, while at the same time maintaining the same power output yet low CO, by reducing combustion residence time, *inter alia*, through control of the location of the homogeneous combustion wave.

Background:

Gas turbines are used for a variety of purposes, among them: motive power; gas compression; and generation of electricity. The use of gas turbines for electrical generation is of particular and growing interest due to a number of factors, among them being modularity of design, generation output capacity to size and weight, portability, scalability, and efficiency. In addition, gas turbines generally use low sulfur hydrocarbon fuels, principally natural gas, which offers the promise of lower sulfur oxides or SO_x pollutant output. This is particularly important in urban areas that use, or can use, gas turbines for power generation, as they are attractive for power-grid supply in-fill to cover growing power needs as urban densification occurs.

Gas turbines tend to operate with a high turbine inlet temperature, in the range of from about 1100 °C for moderate efficiency turbines, to 1500 °C for modern high efficiency engines. To achieve these temperatures at the turbine inlet, the combustion system must produce a somewhat higher temperature, generally 1200 to 1600 °C as a result of some air addition due to seal leakage or the purposeful addition of air for cooling of portions of the gas turbine structure. At these temperatures, the combustion system will produce NO_x. The amount of NO_x produced increases as the temperature increases. However, to meet ever more stringent emissions standards, turbine operating conditions must be controlled so that the amount of NO_x produced does not increase.

A typical gas turbine system comprises a compressor upstream of, and feeding compressed air to, a combustor section in which fuel is injected and burned to provide hot gases to the drive turbine located just downstream of the combustor. **Fig. 1** shows such a prior art system employing a catalytic combustion system in the combustor section. Figure 1 shows a

conventional system of the type described in US patent 5,183,401 by Dalla Betta et al., US 5,232,357 by Dalla Betta et al., US 5,250,489 by Dalla Betta et al., US 5,281,128 by Dalla Betta et al., and US 5,425,632 by Tsurumi et al. These types of turbines employ an integrated catalytic combustion system in the combustor section. Note the combustor section comprises the apparatus system between the compressor and the drive turbine.

As shown in **Fig. 1** the illustrative combustor section comprises: a housing in which is disposed a preburner; fuel source inlets; catalyst fuel injector and mixer; one or more catalyst sections; and a post catalyst reaction zone. The preburner burns a portion of the total fuel to raise the temperature of the gas mixture entering the catalyst, and some NO_x is formed there. Additional fuel is introduced downstream of the preburner and upstream of the catalyst and is mixed with the process air by an injector mixer to provide a fuel/air mixture (F/A mixture). The F/A mixture is introduced into the catalyst where a portion of the F/A mixture is oxidized by the catalyst, further raising the temperature. This partially combusted F/A mixture then flows into the post catalyst reaction zone wherein auto-ignition takes place a spaced distance downstream of the outlet end of the catalyst module. The remaining unburned F/A mixture combusts in what is called the homogeneous combustion (HC) zone (within the post catalyst reaction zone), raising the process gases to the temperature required to efficiently operate the turbine. Note that in this catalytic combustion technology, only a portion of the fuel is combusted within the catalyst module and a significant portion of the fuel is combusted downstream of the catalyst in the HC zone.

Each type of drive turbine has a designed inlet temperature, called the design temperature. For proper operation of a gas turbine at high efficiency, the system or operator must control the outlet temperature of the combustor section to keep the temperature at the design-temperature of the drive turbine. This can be a very high temperature, in the range of 1100°C for moderate efficiency gas turbines and as high as 1400 to 1600°C for modern high efficiency engines. As shown in **Fig. 1**, at these high temperatures, NO_x forms in the "Post catalyst reaction zone" of the combustor section. Although the NO_x level produced in the post catalytic combustion zone is typically low for natural gas and similar fuels, it is still desirable to reduce this level even further to meet increasingly stringent emissions requirements.

Fig. 2 shows the relationship between the temperature in the post catalyst reaction zone and the amount of NO_x produced, for a catalytic combustion system of the type shown in **Fig. 1**. At temperatures below about 1450 °C, identified in the figure as **Region A**, the level of NO_x produced is below 1 ppm. As seen in **Fig. 2**, at temperatures above about 1450 °C, the **Region B** lower boundary, the NO_x level rises rapidly, with 5 ppm produced at 1550 °C, and even higher levels above that temperature, on the order of 9 – 10 ppm or higher.

The formation of NO_x at a high temperature is a kinetically controlled process. A portion of the NO_x, called "Prompt NO_x," or "Fennimore NO_x," forms in the region of the combustor where rapid reactions occur. The amount of Prompt NO_x formed depends on the fuel-to-air ratio and final flame temperature, but this Prompt NO_x stops forming once the flame-front has consumed most of the fuel. A second pathway to the formation of NO_x is the "Thermal NO_x" or "Zeldovich pathway," in which NO_x is formed continuously at high temperatures and in quantities dependant only on time and temperature. In typical gas turbine systems with residence times in the range of 10 to 20 ms (milliseconds), the prompt and thermal pathways produce roughly the same amount of NO_x.

In most combustion processes, reaction of the fuel occurs in a flame that is fixed in location by a flame holder. The flame holder can be either a physical object or an aerodynamic process to anchor or stabilize the flame. Physical elements include bluff bodies, v-gutters, or other such mechanical parts that recirculate the gas stream to stabilize the flame. Aerodynamic stabilizers include physical elements such as swirlers and vanes and such modifications as expanded flow area to stabilize the flame. Flame temperature, temperature profile, physical dimensions of the combustor, and other such features determine the thermal NO_x formation. For example, the designer cannot change thermal NO_x levels without changing the volume or length of the combustor or the position at which the combustor design anchors the flame.

In the case of a catalytic combustion system using the technology described in the above-identified U S Patents, and other references, only a portion of the fuel is combusted within the catalyst and a significant portion of the fuel is combusted down stream of the catalyst in a post catalyst homogeneous combustion (HC) zone. **Fig. 3** schematically illustrates the downstream HC zone.

The top portion of **Fig. 3** is an enlarged schematic of a portion of **Fig.1** showing the major components of a catalytic combustion system 12 located downstream of the preburner. The catalytic combustion system includes a catalyst fuel injector 11, one or more catalyst sections 13 and the post catalyst reaction zone 14 in which is located the HC (homogeneous combustion) zone 15. The bottom portion of **Fig. 3** illustrates the temperature profile and fuel composition of the combustion gases as they flow through the combustor section described above. Temperature profile 17 shows gas temperature rise through the catalyst unit as a portion of the fuel is combusted. After a delay, called the ignition delay time 16, the remaining fuel reacts to give the full temperature rise. In addition, the corresponding drop in the concentration of the fuel 18 along the same path is shown as a dotted line.

As shown in the bottom portion of **Fig. 3**, a portion of the fuel is combusted, without flame, in the catalyst resulting in an increase in temperature of the gas mixture. The mixture

exiting the catalyst is at an elevated temperature and contains the remaining unburned fuel in air. This hot fuel and air mixture autoignites in a homogeneous combustion process in which the remaining fuel reacts in a radical reaction process to form the final reaction products of CO₂ and H₂O, and the temperature rises to the final combustion temperature for the total entering fuel and air mixture.

There is a similar problem with CO in the combustor output gases, in that regulations currently require less than about 100 ppm, and the movement is toward 10 ppm or less. A concern is that in reducing NO_x levels, there may be a countervailing CO increase, such that in order to meet NO_x limits, CO is exceeded. Thus, finding the window of low NO_x and acceptable CO is increasingly difficult at the high **Region B** temperatures needed for efficient energy extraction.

Accordingly, for gas turbines that require combustor outlet temperatures in **Region B** in order to achieve the required drive-turbine design temperatures, and where emissions requirements demand NO_x emissions levels below 3 ppm and CO on the order of 50 - 100 ppm or less, there is a need in the art for better control of the combustion process and ignition timing, and for improved combustion systems, apparatus and controls, in order to ensure that the NO_x level produced in the combustion section of a gas turbine system can be maintained at lower levels, for example, 2 ppm or less while maintaining CO below about 10 ppm.

THE INVENTION

Summary, Including Objects and Advantages:

The invention comprises methods and apparatus, both devices and systems, for control of Zeldovich (thermal) pathway NO_x production in catalytic combustion systems, and more particularly to control of NO_x produced during combustion of liquid or gaseous fuels in the post catalytic sections of gas turbines by reducing combustion residence time in the HC zone through control of the HC wave, principally by adjusting the catalyst inlet temperature.

The invention arises out of the discovery that in the typical combustor having a physical or aerodynamic flame holder, the fuel and air mixture is combusted in a fixed position and does not move significantly as process conditions are varied. In contrast moreover, it has been discovered, unexpectedly, that in a catalytic combustor system, the location of the post-catalyst homogeneous combustion process that results in a temperature rise is not connected to the physical process or fixed flame holder, but rather is controlled by the catalyst exit gas conditions. Accordingly, the process of the invention comprises controlling the catalyst outlet temperature, which changes the HC wave location, which in turn controls the time period (residence time) during which the flame produces thermal NO_x. As soon as the gas mixture enters the drive turbine, work is extracted and the gas temperature drops significantly and NO_x

formation stops. Thus, in accord with the invention, by reducing the residence time at high post-catalyst reaction temperatures, NO_x can be reduced to <3 ppm, preferably <2 ppm, while CO is maintained to within acceptable limits of < 50 - 100 ppm, and even to <5 - 10 ppm.

This inventive feature is illustrated in **Fig. 4**, which shows a series of simple schematic drawings of a catalyst combustor system having a fuel injector, catalyst and post-catalyst homogeneous combustion zone feeding hot gas into a drive turbine. This series of figures illustrates schematically the change in the position of the homogeneous combustion wave, starting in **Fig. 4A**, with the HC wave being shown positioned downstream of the catalyst. The actual physical location of the HC wave is function of the ignition delay time, t_{ignition} , as shown in **Fig. 3**, and the gas velocity. In **Fig. 4B**, the ignition delay is adjusted to be very long, so that after the ignition occurs and the high temperature is reached, the time that the gas mixture will be hot enough for thermal NO_x formation is relatively short and NO_x formation will be minimized. In **Fig. 4A** the ignition delay time is at an intermediate value and in **Fig. 4C** the ignition delay time is very short. In each of these later cases, the Zeldovich pathway NO_x formation is progressively higher due to progressively longer times in which the gas mixture is at the high post-combustion temperature.

The catalyst outlet temperature can be changed by changing the operating conditions of the combustor system. For example, in a first embodiment of the control aspects of the invention, the amount of fuel fed to the preburner (shown in Figure 1) is reduced, then the temperature entering the catalyst module will be lower and the temperature at the exit of the catalyst will also be lower. This lower temperature at the catalyst exit will move the homogeneous combustion wave farther downstream from the catalyst and closer to the turbine, thus reducing the level of thermal NO_x formed. Similarly, increasing the fuel to the preburner will increase the catalyst outlet temperature, move the homogenous combustion wave upstream and increase the amount of thermal NO_x formed. Other control embodiments are described below in the Detailed Description section of this Application.

The inventive control of the location of the HC Wave to reduce the thermal NO_x output is an unexpected and very unusual aspect of catalytic combustion systems employing the partial downstream combustion technology described here.

Brief Description of the Drawings:

The invention is described by reference to the drawings in which:

Fig. 1 is a schematic diagram of a typical prior art gas turbine showing the major components and using an integrated catalytic combustion system in the combustor section;

Fig. 2 is a graph of NO_x produced vs Temperature in a catalytic combustion system and

showing low temperature, low NO_x Region A, and the rapid increase in NO_x produced in Region B above about 1450 °C;

Fig. 3 is a schematic diagram of a catalytic combustion system showing the post catalyst homogeneous combustion zone (HC Zone) located downstream of the catalyst in which the remaining portion of the fuel is combusted ;

Fig. 4 is a multi-part schematic diagram of a catalytic combustion system showing changes in the position of the homogeneous combustion wave (HC Wave) in accord with the invention, **Fig. 4A** showing a general location, **Fig. 4B** showing long ignition delay moves the HC Wave further downstream toward the outlet to the turbine, and **Fig. 4 C** showing shortening the ignition delay moves the HC Wave toward the catalyst module;

Fig. 5 is a partial section, diagrammatic views of the test rig;

Fig. 6 is a graph of test results using the test rig of **Fig. 5** showing NO_x emissions as a function of residence time after essentially complete combustion of the fuel in the HC Zone;

Fig. 7 is a schematic diagram of a portion of the combustor down stream of the catalyst module showing exemplary locations for ultraviolet sensors in the post-catalyst reaction zone; and

Fig. 8 is a graph of the CO concentration profile, in ppm CO vs Residence Time, in the post catalyst reaction zone.

Detailed Description, Including the Best Mode of Carrying Out the Invention:

The following detailed description illustrates the invention by way of example, not by way of limitation of the principles of the invention. This description will clearly enable one skilled in the art to make and use the invention, and describes several embodiments, adaptations, variations, alternatives, and uses of the invention, including what are presently believed to be the best modes of carrying out the invention.

In this regard, the invention is illustrated in the several figures and tables, and is of sufficient complexity that the many parts, interrelationships, process steps, and sub-combinations thereof simply cannot be fully illustrated in a single patent-type drawing or table. For clarity and conciseness, several of the drawings show in schematic, or omit, parts or steps that are not essential in that drawing to a description of a particular feature, aspect or principle of the invention being disclosed. Thus, the best mode embodiment of one feature may be shown in one drawing, and the best mode of another feature will be called out in another drawing. Process aspects of the invention are described by reference to one or more examples or test runs, which are merely exemplary of the many variations and parameters of operation under the principles of the invention.

Fig. 5 shows a catalyst module 13, having two stages in series, of the type shown in US Patent 5,512,250, installed in a tubular test rig 70. Ambient air 72 is introduced at one end and hot exhaust gases exit the test rig at outlet 74 off one leg of an observation Tee 76. A thermocouple 78 measured the temperature of the air just downstream of an electric air heater 80. Thermocouples 82a and 82b were installed upstream and downstream of the catalyst module 13, respectively, to measure the gas temperature both upstream and just downstream of the catalyst module. Additional thermocouples 84 were located spaced various distances downstream of the catalyst module to progressively measure the temperatures of the gas in the homogeneous combustion zone downstream of the catalyst section. In addition, two water-cooled gas-sampling probes, P1 and P2, were installed in the reactor to measure the composition of the gas stream at the position thirty-three cm (P1) and fifty-three cm (P2) downstream of the catalyst. Fuel was supplied to preburner 86, and catalyst fuel 88 was introduced just upstream of a series of static mixers 90 to insure thorough Fuel/Air mixing.

The test sequence was as follows:

1. Set air flow 7900 SLPM (standard liters per minute) and the pressure to 209 psig.
2. Set air temperature to about 450°C.
3. Increase fuel flow necessary for post-catalyst reaction-zone temperature of 1400°C.
4. Vary the catalyst inlet temperature and the fuel flow to cover a variety of combustor outlet temperatures and to move the homogeneous combustion wave to various locations in the post-catalyst reaction-zone.
5. At each point where stable operation is obtained, hold the operating conditions constant and measure the concentration of NO_x (NO plus NO₂), O₂, and CO₂.
6. The NO_x concentrations are then corrected to 15% O₂ concentration by applying the equation (1) below where "ppm (test)" is the measured value of NO_x, "O₂" is the concentration of O₂ at that measurement condition and "ppm (15% O₂)" is the NO_x concentration corrected to 15% O₂.
7.
$$\text{NO}_x (\text{ppm at } 15\% \text{ O}_2) = \text{NO}_x (\text{ppm at test condition}) \times (20.9 - 15)/(20.9 - \text{O}_2),$$
 Equation 1, with the results being shown in Fig. 6, NO_x emissions in ppm as a function of the residence time after essentially complete combustion of the fuel.

The residence time shown for the different curves of Fig. 6 is the time from: 1) the point where most of the fuel has combusted and the temperature has risen to approximately the maximum post-catalyst reaction zone temperature, and 2) the point at which the gas sample is taken for measurement of the NO_x level. The test was run by determining the homogeneous combustion wave location and then moving the location of this combustion wave by changing the inlet temperature of the fuel/air mixture to the catalyst by changing the power to the electric

air heater that heats the air in the test rig. As the catalyst inlet gases temperature is changed, the total fuel to the catalyst was changed to maintain a constant post-catalyst reaction zone temperature. As the fuel/air mixture inlet temperature (F/A temperature into the catalyst) is reduced, the homogeneous combustion wave moves downstream and shortens the residence time at high temperature. As the fuel/air mixture inlet temperature (F/A temperature into the catalyst) is increased, the homogeneous combustion wave moves toward the catalyst module and the residence time at high temperature increases. Over the entire temperature range studied, limiting the residence time to lower values reduces the NOx significantly. For example, at 1540°C, the NOx is reduced from 4.6 ppm to about 3 ppm or a reduction of 35%. At lower temperatures, the NOx level is lower, but operation at lower residence time still reduces the level of NOx.

On a gas turbine, the process by which the position of the homogeneous combustion wave can be controlled depends on the design of the catalytic combustion system. Where the catalyst inlet temperature is controlled by a flame burner, then the catalyst inlet temperature is controllable by changing the fuel flow to the flame burner. For example, in a fuel distribution proportioning embodiment of the invention, to decrease the level of NOx formed at a given turbine power output level where the drive turbine inlet temperature is to be held constant, the fraction of fuel fed to the preburner is decreased and the fraction of fuel fed to the catalyst fuel injector increased, so the total fuel fed to the gas turbine is held constant. Thus, by this proportional fuel flow control aspect of the invention, the total power output can be constant, yet since the fuel fed to the preburner has been decreased, the catalyst inlet and outlet temperatures are decreased and the homogeneous combustion wave is moved downstream to decrease the residence time at high temperature and the NOx level.

Other suitable processes for controlling catalyst inlet temperature will be evident to those skilled in the art for other combustor designs and for other combustion processes. Alternatively, holding the catalyst inlet temperature constant and varying the fuel to the catalyst also results in moving the homogeneous combustion wave. While this will also change the post-catalyst reaction zone temperature, that temperature change may be within an acceptable range for some combustion processes.

Additional embodiments of the inventive system and method that can be used to advantage in a system that is designed for, or takes advantage of, the control of the residence time at high temperature to control NOx, include the following:

- As shown in **Fig. 7**, one or more flame sensors 92 can be installed downstream of catalyst module in the post-catalyst combustion zone 14 of the combustor section 12 that are sensitive to the homogeneous combustion wave. For more detail on the location

and use of sensors, particularly optical sensors, in connection with control of gas turbines employing catalytic combustion systems, see our co-pending application USSN 09/942,976, filed August 29, 2001, entitled CONTROL STRATEGY FOR FLEXIBLE CATALYTIC COMBUSTION SYSTEM, the disclosure of which is hereby incorporated by reference. Exemplary sensors include various types of ultraviolet sensors that are sensitive to the radiation produced from at least some of the radical reactions that occur in the radical reaction process for hydrocarbon and other fuels. Such a UV sensor, such as 92a can be oriented to "look at" the outlet end of the catalyst module to protect it from over-temperature, as where the HC Wave encroaches on the catalyst module. A preferred position for a sensor is downstream adjacent the outlet to the turbine, as shown at the right of Fig. 7, where sensor 92b is positioned to be exposed to the homogeneous combustion wave when it is in the desired location. The signal of this sensor, or a series of such sensors disposed parallel to the longitudinal axis of the combustion zone, can then be used to control the combustion process, in particular to control the catalyst inlet temperature, e.g., by control of the F/A mixture entering the catalyst in accord with the inventive process to hold the homogenous combustion process in a particular, predetermined, desired location in order to limit the formation of NO_x to a preselected level, e.g., to <3 ppm, preferably below about 2 ppm, and most preferably below about 1 ppm.

- A second type of sensor that can be used in a manner, and located in positions, similar to the above ultraviolet-type sensor, is an ion sensor whose signal is some function of the concentration of ionized gas molecules in the region near the sensor. Such sensors typically measure ion current between a pair of electrically charged plates or electrodes. Such a sensor, or array of suitably located sensors, can be positioned in the post catalyst reaction zone to monitor the location of the homogeneous combustion wave.

- Thermocouples can be located in post-catalyst reaction zone to measure gas temperature and thus the location of the homogeneous combustion wave, since the gas temperature rises substantially at the location of this combustion wave. Alternatively, thermocouples can be positioned to measure the combustion zone wall temperature (typically metal walls). Since the metal wall is in heat transfer relationship with the hot gases, the temperature rise in the gas at the location of the homogeneous combustion wave would be reflected as a corresponding temperature rise in the metal wall temperature.

- In cases where all of the operating parameters of the system are well understood and the important system parameters can be measured, then an empirical model of the combustor can be used to calculate the location of the HC Wave. This calculated value is then used in a control system algorithm to control the location of the HC Wave. This is an

example of a "model based control strategy".

• As the combustion wave moves very close to the combustor outlet or (turbine inlet), the CO level in the turbine exhaust may increase due to the fact that the reaction time in the HC Wave is too short to obtain complete reaction of the CO (oxidation to CO₂) within the combustor burnout zone. The CO concentration entering the drive turbine and also exiting the turbine exhaust will be as shown in **Fig. 8**, which is derived for a selected set of turbine and catalytic combustor operating conditions. The "knee" in the curve is at approximately 10 ppm CO, 13 ms Residence Time. Shorter residence times cause the CO to rapidly increase, while longer residence times can reduce the CO output to <10 ppm as shown in the curve. However, this is counter to the NOx curve, in that the shorter residence time means the HC Wave is closer to the catalyst unit with a corresponding longer residence time at high temperature in the post catalytic reaction zone, and more NOx is produced. Thus, the invention provides principles by which the operating parameters are adjusted by the controller to achieve this very difficult low NOx/low CO/high Power Output target window. Controlling the gas turbine so that the CO concentration is on the curve of **Fig. 8**, below about 100 ppm, and preferably in the vicinity of the knee in the curve of **Fig. 8**, <10 ppm and most preferably <5 ppm, still permits the HC Wave to be maintained at the desired location (residence time short, ignition delay long) for low NOx production. Thus, monitoring the CO level with CO sensors can be used to control the position of the HC Wave. The sensor 92b shown in **Fig. 7** can be a CO breakthrough sensor, the readings of which are monitored and fed back to the controller, e.g., for F/A adjustment to control the HC Wave location. Alternatively, the CO sensor can measure the CO in the turbine exhaust (see **Fig. 1**) and the CO level sensor signal used as an input to a controller for control of the position of the HC Wave. One exemplary control strategy is to periodically change the combustor operating conditions so that the HC Wave is moved closer to or further away from the post catalyst reaction zone exit and monitor the CO level in the turbine exhaust. In this manner, the optimum operating conditions corresponding to a CO level in the range of 5 or 10 ppm CO can be determined and the turbine then can be controlled at this operating condition using an operating line control strategy as described in the aforesaid co-pending application SN 09/942,976 filed August 29, 2001, the disclosure of which is hereby incorporated by reference.

• Similarly, one or more NOx sensors in the HC Zone can be employed in locations as described above for **Fig. 7**. The sensor outputs are used to control the hot turbine inlet

gases to a specified NO_x level by controlling the above-described parameters that adjust the position of the homogeneous combustion wave.

The actual location of the homogeneous combustion wave can be controlled by varying the following system or operating parameters:

- a. Changing the catalyst inlet temperature;
- b. Changing the fraction of air bypassing the catalyst to thus change the fuel/air ratio through the catalyst. Since the total turbine air flow and total turbine fuel flow is not changed, the turbine inlet temperature and load operating point will remain the same;
- c. Adjusting the air to the preburner, e.g., by overboard bleed of compressor discharge air upstream of the preburner which increases the fuel air ratio of the mixture in the catalyst and changes the position of the homogenous combustion wave;
- d. Changing the composition of the fuel mixture by adding or removing components that would effect the ignition delay time. Longer chain hydrocarbons or hydrogen, for example, will shorten the ignition delay time;
- e. Addition of water to the compressor inlet or to the combustor to increase total mass flow and thus modify the gas velocity and other operating conditions and thus change the position of the homogeneous combustion wave; and
- f. Fuel distribution proportioning as between the preburner and the catalyst module.

INDUSTRIAL APPLICABILITY:

It is clear that the process and apparatus of the invention will have wide industrial applicability, not only to catalytic combustion systems for gas turbines, but also to combustors employed in a variety of other types of power and hot gas producing systems, such as industrial boilers for steam and process heat.

The reduction in NO_x while maintaining CO within acceptable limits and not sacrificing power output under the inventive process and apparatus is environmentally beneficial, offering the potential for significant amelioration in NO_x produced by high temperature combustion processes, thus lending the invention a wide industrial applicability.

It should be understood that one of ordinary skill in the art can make various modifications within the scope of this invention without departing from the spirit thereof. It is therefore wished that this invention be defined by the scope of the appended claims as broadly as the prior art will permit, and in view of the specification if need be.

CLAIMS:

1. In a method of combustion of a fuel/air mixture in a combustor having a catalytic combustion system containing a catalyst unit and wherein a portion of the fuel is combusted in a homogeneous combustion wave (HC Wave) downstream of said catalyst unit, said HC Wave being located in a post-catalyst reaction zone, said combustion producing hot combustion gases from which energy is extracted, the improvement comprising:

a) controlling the location of said HC Wave in said post-catalyst reaction zone to reduce the time at which said hot gas is retained in said post-catalyst reaction zone before extraction of energy therefrom to reduce the NO_x produced in said post-catalyst reaction zone.

2. A reduced NO_x combustion process as in claim 1 wherein said NO_x is reduced to below about 3 ppm in hot combustion gases having a temperature in the range of above about 1450 °C while maintaining the CO within the range of below about 100 ppm.

3. A reduced NO_x combustion process as in claim 2 wherein said combustor is part of a gas turbine system that includes a compressor upstream of said combustor providing compressed air to said combustor.

4. A reduced NO_x combustion process as in claim 1 wherein said controlling step includes monitoring at least one condition of at least one of said fuel/air mixture and said hot combustion gas.

5. A reduced NO_x combustion process as in claim 4 wherein said condition monitoring includes sensing at least one of fuel amount, fuel feed rate, fuel/air temperature, gases temperature, NO_x, and CO.

6. A reduced NO_x combustion process as in claim 5 wherein said NO_x and CO is monitored and the location of said HC Wave is controlled to reduce NO_x while maintaining CO within a predetermined range.

7. A reduced NO_x combustion process as in claim 1 wherein said controlling step includes adjusting the catalyst outlet gas temperature to control the delay time for ignition of the fuel in the HC Wave.

8. A reduced NO_x combustion process as in claim 7 wherein said catalyst outlet gas temperature is adjusted by controlling the temperature of the fuel/air mixture entering the catalyst.

9. A reduced NO_x combustion process as in claim 8 wherein said combustor includes a preburner upstream of said catalyst unit and said temperature of at least one of said fuel/air

mixture and outlet gas is controlled by at least one of:

- a) adjusting the fraction of air bypassing the catalyst;
- b) adjusting the fuel supplied to said combustor by proportioning the fuel supplied between said catalyst and said preburner;
- 5 c) adjusting air input to said preburner;
- d) changing the composition of the fuel by introduction of components that affect the ignition delay time; and
- e) addition of water in at least one of upstream of said combustor and in said combustor.

10 10. A reduced NOx combustion process as in claim 9 wherein the temperature of said hot combustion gas is maintained in a predetermined range for energy extraction and the fuel supplied to said preburner is controlled to move said HC Wave to a location to reduce NOx while maintaining CO to within a predetermined range of below about 50 ppm in said hot gas.

15 11. A reduced NOx combustion process as in claim 3 wherein said controlling step includes developing an empirical model of the operation of said combustor under a range of operating parameters, calculating the location of the HC Wave in the post-catalyst reaction zone as said parameters change, and setting system operating controls to selectively position the location of the HC Wave.

20 12. Apparatus for control of NOx produced during combustion of a fuel/air mixture in a combustor having a catalytic combustion system disposed medially therein and a post-catalyst combustion zone extending downstream of the catalyst of said catalytic combustion system, and a portion of the fuel is combusted in a homogeneous combustion wave (HC Wave) in said post-catalyst combustion zone, said combustion producing hot combustion gases from which energy is extracted, the improvement comprising:

25 a) at least one sensor mounted in association with said post-catalyst combustion zone, said sensor outputting a signal responsive to at least one of said HC Wave, NOx, temperature and CO; and

b) a controller receiving and processing said signal to control the location of the HC Wave to reduce the NOx produced in said post-catalyst combustion zone while maintaining CO levels to within a predetermined range in said hot gas.

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13. NOx control apparatus as in claim 12 wherein said combustor is part of a gas turbine system that includes a compressor upstream of said combustor providing compressed air to said combustor and said NOx is reduced to below about 3 ppm in hot combustion gases having a temperature in the range of above about 1450 °C, and CO is maintained below about 100 ppm.

14. NOx control apparatus as in claim 12 wherein said controller adjusts the temperature of the catalyst inlet fuel/air mixture to control the location of said HC Wave.

15. NOx control apparatus as in claim 12 wherein said sensors are disposed in an array along at least a portion of said post-catalyst reaction zone to provide a profile of the sensed value in said zone.

16. NOx control apparatus as in claim 12 that includes at least one said sensor disposed in association with said combustor upstream of said catalyst.

17. NOx control apparatus as in Claim 12 wherein said at least one sensor is selected from at least one of a flame sensor, a UV sensor, an ion sensor, a CO sensor, and a temperature sensor.

18. NOx control apparatus as in claim 17 wherein at least one sensor is oriented to look at the downstream end of said catalyst.

19. NOx control apparatus as in claim 14 wherein said controller effects positioning of said HC Wave by:

- a) adjusting the fraction of air bypassing the catalyst;
- b) proportionally feeding fuel supplied, between said catalyst and a preburner upstream of said catalyst in said combustor;
- c) adjusting air input to said preburner;
- d) feeding fuel into said combustor having components that selectively affect the ignition delay time; and
- e) addition of water in at least one location selected from upstream of said combustor and in said combustor.

20. NOx reduction apparatus as in claim 13 wherein said controller includes an a control algorithm derived from an empirical model of the operation of said combustor under a range of operating parameters, said algorithm including calculated locations of the HC Wave in the post-catalyst reaction zone in relation to change in said parameters, and said controller sets system operating controls to selectively position the location of the HC Wave in response to at least one of selected hot combustion gas output temperature, NOx upper limit, and CO upper limit.

ABSTRACT

Methods and apparatus, both devices and systems, for control of Zeldovich (thermal) NO_x production in catalytic combustion systems during combustion of liquid or gaseous fuels in the post catalytic sections of gas turbines by reducing combustion residence time in the HC zone through control of the HC Wave, principally by adjusting the catalyst inlet temperature. As the fuel/air mixture inlet temperature (to the catalyst) is reduced, the HC Wave moves downstream (longer ignition delay time), shortens the residence time at high temperature, thereby reducing thermal NO_x production. The countervailing increase in CO production by longer ignition delay times can be limited by selectively locating the HC Wave so that thermal NO_x is reduced while power output and low CO production is maintained. NO_x is reduced to on the order of <3 ppm, and preferably <2 ppm, while CO is maintained <100 ppm, typically <50 ppm, and preferably <5 – 10 ppm.

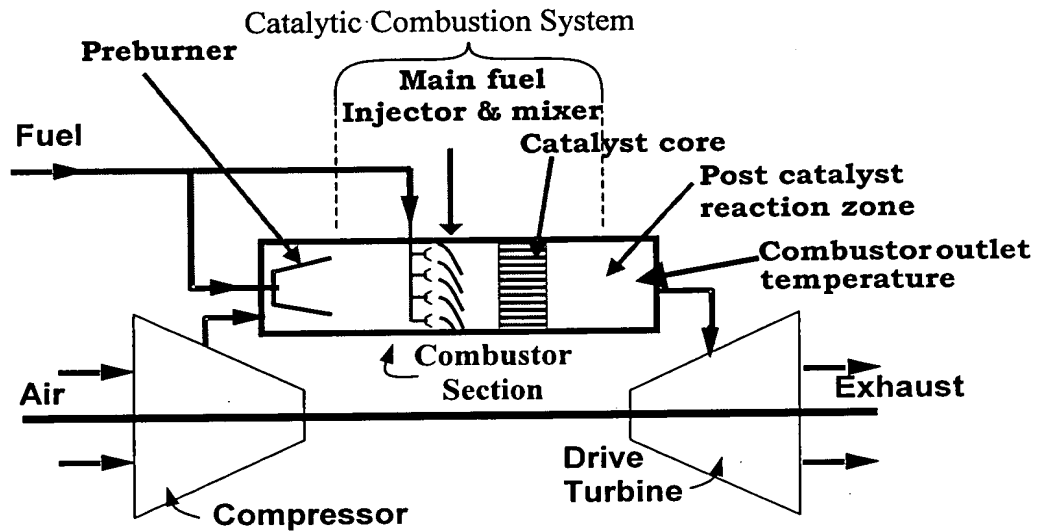


Figure 1, Prior Art

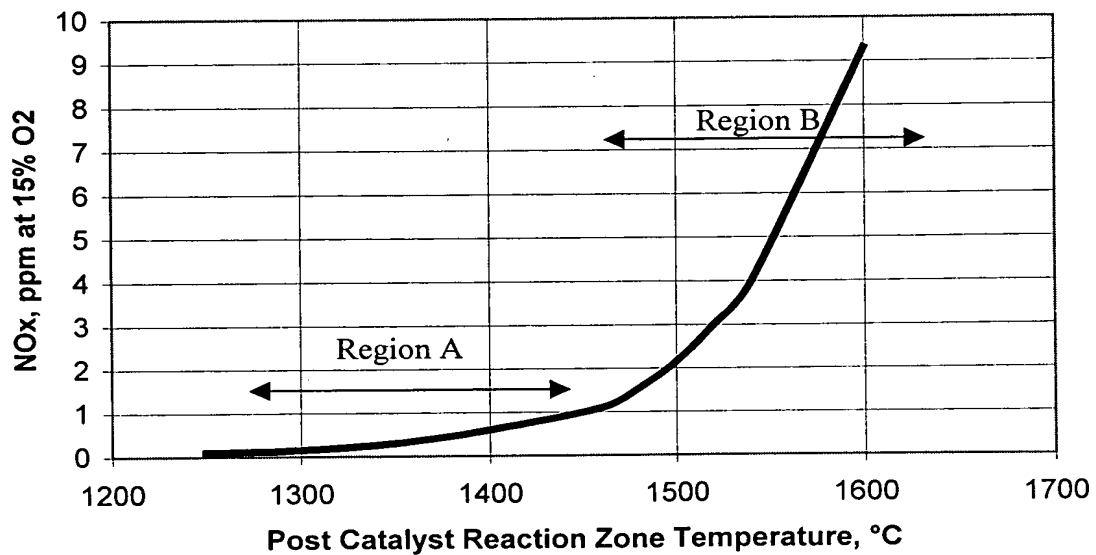


Figure 2, NOx produced vs. Temperature in a catalytic combustion system

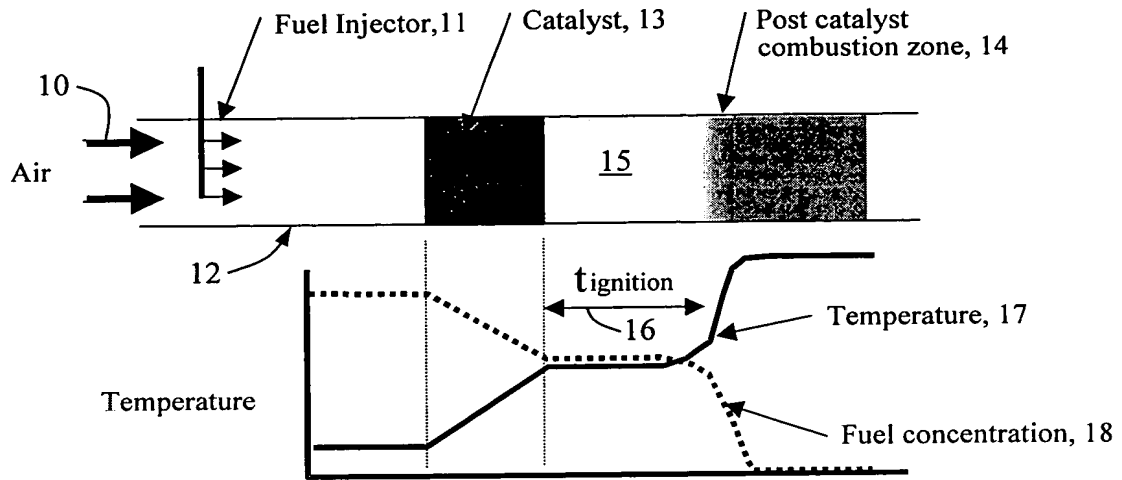


Fig. 3

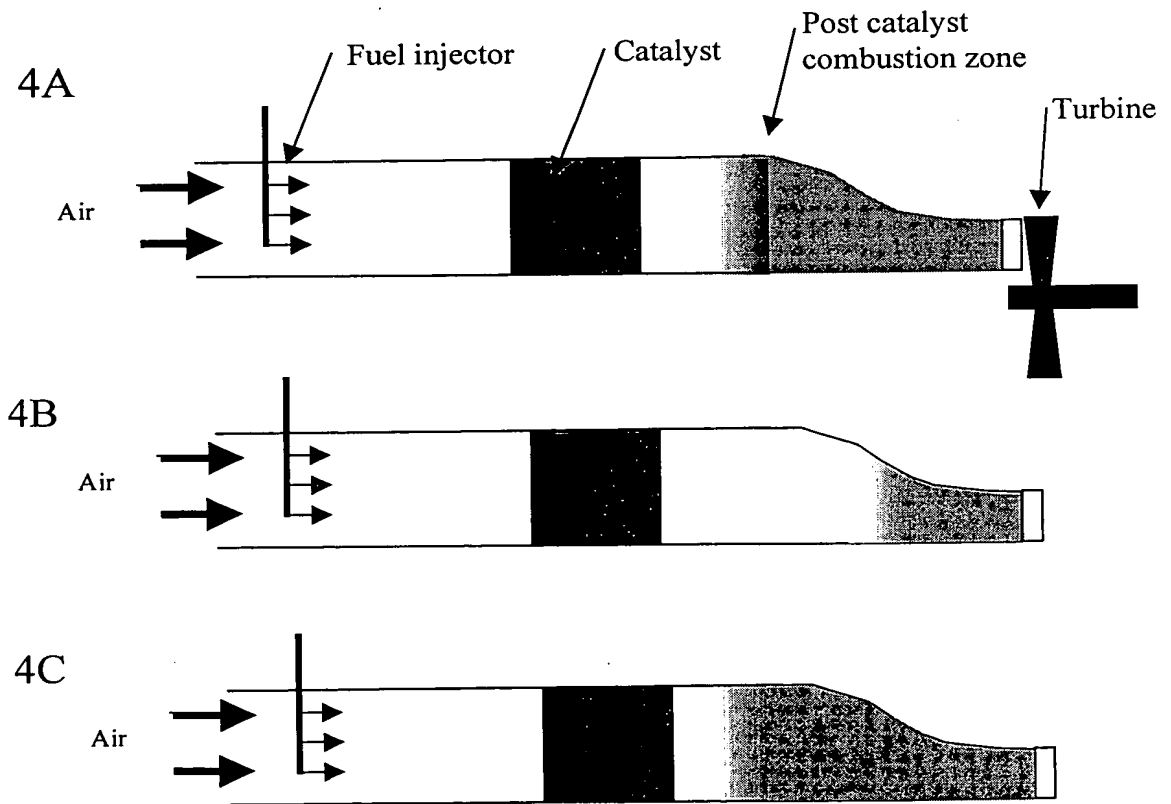


Fig. 4

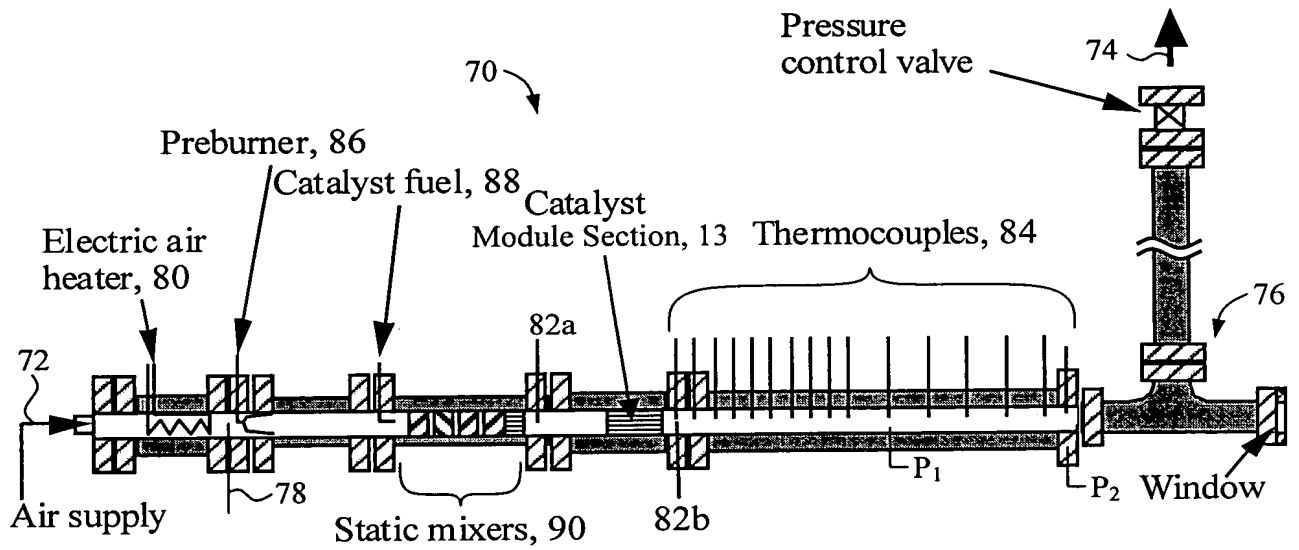


Fig. 5

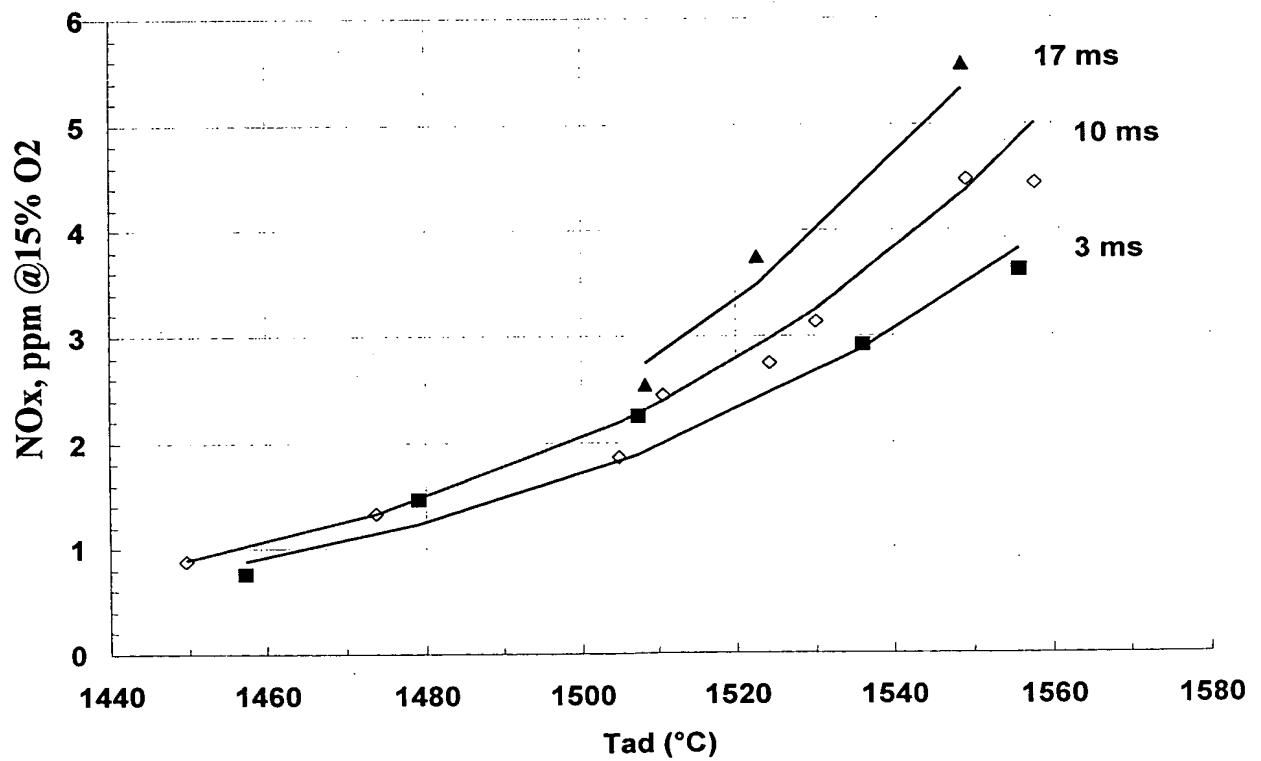
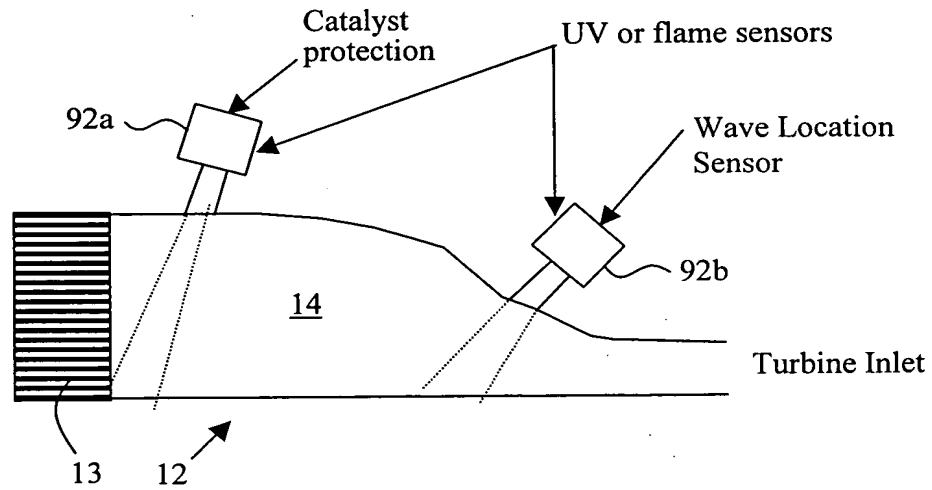
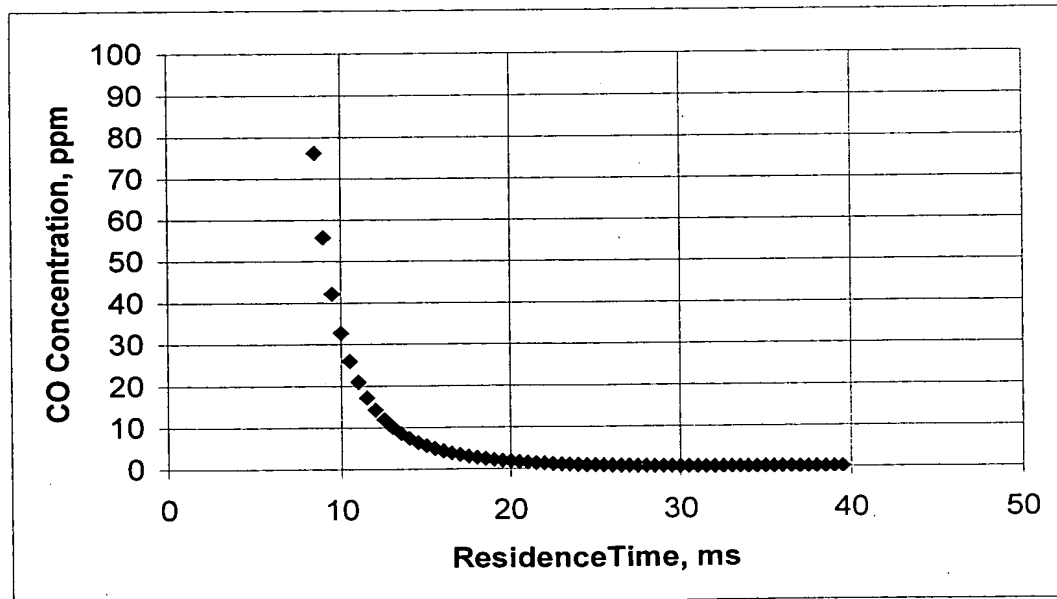


Fig. 6

*Fig. 7**Fig. 8*